

Coprocessing of 4-(1-naphthylmethyl)biphenyl with Waste Tires Using Finely Dispersed Iron and Molybdenum Catalysts

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ABSTRACT

Coliquefaction of waste tires with coal is a feasible method for upgrading both materials. To evaluate the effect of waste tires on reactions that occur during liquefaction, waste tire and carbon black, a component of tires, were reacted in the presence of 4-(1-naphthylmethyl)biphenyl (NMBB), a model coal compound known to hydrocrack at liquefaction conditions. Waste tires promoted NMBB hydrocracking compared to no additive although carbon black, introduced at the level present in waste tires increased hydrocracking more. Combining Mo naphthenate with waste tire or carbon black had a higher activity for hydrocracking than the corresponding combinations with Fe naphthenate. Selectivity for NMBB cleavage was also different with the two different catalysts. The addition of S increased the activity of Fe naphthenate with waste tire but decreased that of Mo naphthenate. Increased NMBB hydrocracking of 79.9% was obtained by combining Mo naphthenate and carbon black. Combining Fe naphthenate with carbon black or Mo naphthenate did not increase NMBB hydrocracking compared to the values obtained with the individual materials.

INTRODUCTION

Waste tires are waste disposal problems in the United States where more than 240 million tires are disposed of annually. Since waste tires are composed of either natural or synthetic rubber, aromatic oil and carbon black, waste tires are a potential energy source. Waste tires can be coliquefied with coal to produce more valuable end products. Farcasiu et al.^{1,2} demonstrated that coprocessing of used rubber tires and coal produced liquids that are potential sources of transportation fuels or of aromatic oil to be used in new tires. Zondlo and coworkers³ found that the coliquefaction of bituminous coal and rubber tires resulted in greater conversion than did either material individually. Hydrogenation catalysts used by Orr et al.⁴ affected the THF soluble yields of the coliquefied material.

In order to understand more fully how waste tire and carbon black affect the thermal and catalytic reaction of coal at liquefaction conditions, the model species, 4-(1-naphthylmethyl)biphenyl, was used as a model coal compound. In addition, coal and hydrogenation catalysts were used as additives to evaluate their effect on NMBB. The amount and selectivity of the NMBB hydrocracking were used as measures to determine the effect of the different individual additives and combination of additives.

EXPERIMENTAL

Materials. The model NMBB (99% purity) was obtained from TCI America and used as received. The catalysts tested in this study were iron naphthenate (FeNaph) (6% Fe), iron stearate (FeSTR) (9.0% Fe, 98% purity) from Strem, hydrated iron oxide (FeOOH) (63.3% Fe) from Aldrich, and molybdenum naphthenate (MoNaph) (6.0% Mo) from Shepherd Chemical. Three waste rubber samples, GF30 (30 mesh), GF40 (40 mesh) and GF80 (80 mesh), were supplied by Rouse Rubber Industries, Vicksburg, MS. The coal used in the study was Illinois No. 6 bituminous coal from Amoco and carbon black, Black Pearls 2000, was supplied by Cabot Industries. All of the additives to the NMBB reaction were used as received.

Reaction Procedures. Reactions were performed in stainless steel tubular microreactors of ~20 cm³ at 400°C for 30 min with a H₂ pressure of 1250 psig introduced at ambient. The reactor was agitated horizontally at 450 rpm. The reaction system consisted of 0.25 g of NMBB; when additives were used, waste tire, coal or carbon black was added at an equivalent gram amount of 0.25 g. When the relative amount of the additives was changed, the amount of NMBB was held constant and the added material amount was either 5 times 0.25 g or 0.2 times 0.25 g. Catalyst precursors of MoNaph, FeNaph, FeOOH and FeSTR were added at a level of 900 to 1,100 ppm active metal on a per gram of material basis. When dual catalysts of Fe-based precursors and MoNaph were used, the total level of metal was kept constant at 900 to 1100 ppm with Fe:Mo weight ratios of 1:1. When sulfur was added to the reaction, elemental sulfur was added in a 3:1 stoichiometric ratio of sulfur to metal assuming that either Fe₇S₈ or MoS₂ was formed.

The reaction products obtained from reactions of NMBB and the various additives were analyzed by gas chromatography using a Varian Model 3700 gas chromatograph equipped with a fused silica J&W capillary DB-5 30 m column and flame ionization detection. The only products that were analyzed were those from NMBB. The products obtained from NMBB were primarily hydrocracked products; trace amounts of hydrogenated products were detected. Percent

hydrocracking (%HYC) of NMBB was defined as the moles of hydrocracked liquid products as a percentage of total moles of liquid products produced.

RESULTS AND DISCUSSION

Hydrocracking of 4-(1-naphthylmethyl) bibenzyl. The model hydrocracking compound 4-(1-Naphthylmethyl) bibenzyl (NMBB) was reacted noncatalytically and catalytically with and without sulfur in the presence of added material of waste tires, carbon black, and coal as presented in Table 1. A number of different combinations was used to test the effect of the individual additives and combinations of additives on the hydrocracking activity of NMBB. The products produced from NMBB were determined and defined as the lumped parameter, percent hydrocracking. Where NMBB was hydrocracked at the reaction conditions and in the presence of any additive or catalyst used, the primary products obtained were methylbibenzyl (MBB) and naphthalene (NAP). Secondary products, such as naphthyltolymethane (NTM), bibenzyl (BB), methylnaphthalene (MN) and toluene (TOL), were obtained in small amounts as the extent of hydrocracking increased.

The cleavage of NMBB can occur at five different sites which are shown in Figure 1 and are labeled a through e. The selectivity of the bond cleavage that occurred with the different additives is given in Table 1. The primary cleavage that occurred with all of the additives and catalysts was at bond a. In most systems, the second most prevalent cleavage occurred at bond d, with a small amount of cleavage occurring at b. No cleavage was observed at bonds c or e in any of the reactions performed. The selectivity for hydrocracking NMBB at a given bond is given in Table 1 as SA for bond a, SB for bond b and SD for bond d. These selectivities are defined as cleavage at either bond a, b, or d which is divided by the sum of the bond cleavage a, b and d. Therefore, the parameters chosen to compare the results of the different additives and catalysts on NMBB were % HYC, which described the activity for hydrocracking under the specific reaction conditions, and SA, SB, and SD, which reflected the selectivity of the additive or catalyst for NMBB bond cleavage.

Effect of Waste Rubber, Additives and Catalysts on NMBB Hydrocracking. Table 1 presents the effect of different additives and catalysts on NMBB hydrocracking. Initial reactions employed waste tires in three mesh sizes added to NMBB. With increasing mesh size from 30 to 80 and decreasing particle size, the waste tire's effect on NMBB hydrocracking increased from 11.3 to 15.3%. The decreased particle size may have allowed more contact between the reacting NMBB and the active hydrocracking component in waste tire, carbon black. All subsequent experiments were performed with GF 30 waste tire. When the weight ratio of NMBB to waste tire decreased from 1:0.2 to 1:5, the % HYC of NMBB increased from 9.3 to 13.1%, while the selectivity for bond cleavage at a decreased from 91 to 62% with a corresponding increase at d from 9 to 38%. Although the selectivity changed rather substantially with increased waste tire, the change in the total amount of hydrocracking was small.

Since carbon black composes between 20 to 30% of waste tires, the effect of carbon black on the hydrocracking of NMBB was evaluated. Introducing carbon black at a 1:1 weight ratio yielded 79.1% HYC of NMBB. Adding waste rubber or coal at the same level resulted in much less HYC, 11.3 and 7.0%, respectively. A higher ratio of NMBB to carbon black of 1:0.2 was used to approximate the lower amount of carbon black present in waste tire; the amount of HYC achieved was 17.7% which was higher than that obtained with a 1:1 ratio of NMBB to waste tire containing at a minimum 20% carbon black. Likewise, when the ratio of NMBB to waste tire was 1:5 in which carbon black was present in an equivalent amount as in the reaction with a NMBB to carbon black ratio of 1:1, the % HYC was much less yielding 13.1% compared to 79.1%. The carbon black contained in the GF 30 waste tire was not nearly as active as carbon black introduced directly. The selectivity for cleavage at bond a was greater for carbon black than for carbon black in waste tire at equivalent carbon black loadings.

In the coprocessing of waste tire with coal, hydrogenation catalysts would be used to increase the conversion of both coal and waste tire. Two slurry phase hydrogenation catalysts, FeNaph and MoNaph, were used in conjunction with NMBB individually and with additives of waste tire and carbon black. Reactions were performed with and without sulfur. When MoNaph was combined with waste tire, 38.2% HYC of NMBB occurred which was more than double the amount obtained with FeNaph. The addition of sulfur increased the amount of % HYC with FeNaph but decreased the effectiveness of MoNaph. Combining FeNaph or MoNaph with carbon black resulted in high levels of % HYC: 86.4% for FeNaph and 97.9% for MoNaph. The selectivity for cleavage at bond a was greater for Mo than for Fe even when sulfur or carbon black was added.

Ternary systems of NMBB with waste tire and carbon black were reacted without additional catalysts and with three different iron catalysts or MoNaph. The combination of waste tire and carbon black at a 1:0.2:0.2 ratio yielded 29% HYC of NMBB. Addition of MoNaph to this

ternary system increased the % HYC to 71.3% although the selectivity for cleavage at bond a remained high and constant. Increasing the amount of waste tire in the system to a ratio of 1:1:0.2 of NMBB to waste tire to carbon black increased % HYC to an even higher value of 83.5%. Utilization of three types of Fe catalysts at that same ratio resulted in % HYC of 42.6% for FeSTR, 53.7% for FeNaph and 55.2% for FeOOH. All of these hydrocracking values were lower than that obtained for MoNaph.

Reactions with NMBB and waste tires were also performed with combined catalysts containing one of the iron precursors, FeNaph, FeOOH, or FeSTR with MoNaph and sulfur. All three of the reactions yielded % HYC between 16.5 and 20.3% so that the type of iron present made little difference in the hydrocracking behavior of NMBB. The % HYC of 18.5% achieved by the combined catalyst of MoNaph with FeNaph was only slightly higher than the 17.5% HYC yielded by the reaction with FeNaph alone. The selectivity for all of the combined catalysts was very high, ranging from 94 to 98%. The presence of the combined catalysts were not synergistic for promotion of NMBB hydrocracking.

SUMMARY

The NMBB system provided a model for measuring the activity of waste tire and carbon black for hydrocracking. Since NMBB contains C-C bonds that are similar to those present in some coal molecules NMBB can be used to predict the effect of waste tire and carbon black in a liquefaction system containing coal and waste tire. Carbon black introduced directly at coprocessing conditions was highly active for hydrocracking NMBB. When carbon black was present in waste tires, carbon black's activity was much less, indicating that the processing and contact of the carbon black with other material in the waste tires was detrimental to its activity. The combination of MoNaph with either waste tire or carbon black resulted in higher hydrocracking activity and selectivity for cleavage at bond a than did FeNaph. The combination of iron catalysts with MoNaph did not promote hydrocracking of NMBB.

REFERENCES

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Figure 1. Cleavage Sites for 4-(1-Naphthylmethyl)biphenyl.

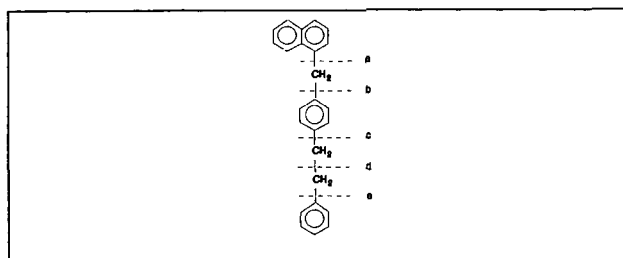


Table 1. Selectivity of the Slurry Catalysts for Hydrocracking 4-(1-Naphthylmethyl)biphenyl

Reaction Systems	%HYC ^b	Cleavage of a+b+d ^c	Selectivity*100%		
			SA	SB	SD
NMBB (thermal)	4.9±1.3	2.5	61	0	39
NMBB+S	9.3±2.7	4.7	66	2	32
NMBB+GF30WT(1:1)	11.3±2.2	5.7	77	0	23
NMBB+GF40WT(1:1)	13.5±2.5	6.8	76	0	24
NMBB+GF80WT(1:1)	15.3±2.4	7.7	81	0	19
NMBB+WT ^a (1:0.2)	9.3±2.1	4.7	91	0	9
NMBB+WT(1:5)	13.1±1.7	6.6	62	0	38
NMBB+CB(1:1)	79.1±2.7	39.6	78	6	16
NMBB+CB(1:0.2)	17.7±2.7	8.9	84	4	12
NMBB+Coal(1:1)	7.0±2.1	3.5	83	0	17
NMBB+FeNaph	5.5±1.0	2.8	79	0	21
NMBB+MoNaph	6.4±0.9	3.3	76	0	24
NMBB+FeNaph+S	15.5±1.4	7.7	86	4	10
NMBB+MoNaph+S	39.4±2.3	19.7	92	5	3
NMBB+WT+FeNaph(1:1)	15.5±2.6	7.8	73	0	27
NMBB+WT+MoNaph(1:1)	38.2±2.2	19.2	95	1	4
NMBB+CB+FeNaph(1:1)	86.4±3.8	43.3	89	4	7
NMBB+CB+MoNaph(1:1)	97.9±2.2	49.0	94	4	2
NMBB+WT+FeNaph+S(1:1)	17.5±2.6	8.8	75	0	25
NMBB+WT+MoNaph+S(1:1)	30.1±2.4	15.1	96	0	4
NMBB+CB+FeNaph+S(1:1)	87.3±3.8	43.7	88	6	6
NMBB+CB+MoNaph+S(1:1)	99.7±1.6	49.8	94	5	1
NMBB+WT+MoNaph+S(1:0.2)	29.4±3.0	14.8	98	0	2
NMBB+WT+MoNaph(1:0.2)	13.8±3.0	6.9	97	0	3
NMBB+CB+MoNaph+S(1:0.2)	79.9±3.6	40.0	95	4	1

Table 1. (Continued)

NMBB+WT+MoNaph(1:5)	23.2±2.4	11.7	69	0	31
NMBB+WT+MoNaph+S(1:5)	18.0±2.1	9.1	67	0	33
NMBB+WT+CB(1:0.2:0.2)	29.0±1.7	14.6	92	3	5
NMBB+WT+CB+MoNaph (1:0.2:0.2, 1000 ppm)	71.3±2.5	35.7	95	4	1
NMBB+WT+CB+MoNaph (1:1:0.2, 1000 ppm)	83.5±2.4	41.8	93	5	2
NMBB+WT+CB+FeNaph (1:1:0.2, 1000 ppm)	53.7±2.5	26.9	89	5	6
NMBB+WT+CB+FeOOH (1:1:0.2, 1000 ppm)	55.2±3.0	27.7	95	2	3
NMBB+WT+CB+FeSTR (1:1:0.2, 1000 ppm)	42.6±2.8	21.4	97	0	3
NMBB+WT+FeNaph+MoNaph+S (1:1, 500 ppm each)	18.5±2.1	9.3	98	0	2
NMBB+WT+FeOOH+MoNaph+S (1:1, 500 ppm each)	20.3±2.2	10.2	96	0	4
NMBB+WT+FeSTR+MoNaph+S (1:1, 500 ppm each)	16.5±3.0	8.3	94	0	6

^aWT=waste tire rubber GF30 unless specified; CB=carbon black; MoNaph=Mo Naphthenate; FeNaph=Fe Naphthenate; FeSTR=FeStearate.

^b%HYC is defined as the moles of hydrocracked liquid products as a percentage of the total moles of liquid products produced.

^cCleavage of Bonds a, b, and d is defined as bond cleavage of bond a, b, and d in NMBB.

^dSelectivity is defined as bond cleavage at a (SA) or b (SB) or d (SD) divided by the combined bond cleavage of a, b, and d.